Synthesis and Characterization of Amphiphilic A_3B_3 Hetero Arm Star Copolymers: Poly(isobutylene$_3$-*star*-methyl vinyl ether$_3$)

Jongpil Yun and Rudolf Faust*

Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854

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Introduction. Asymmetric star polymers are star branched macromolecules having molecular weight, chemical or topological asymmetry among the arms. Until recently, very little was known about their properties due to difficulties in the preparation of these products with high structural uniformity. Lately, many reports appeared on stars with chemical asymmetry (also called hetero- or miktoarm star), such as A_nB_n and A_nB_m, mainly by anionic polymerization. The developments in this field have been reviewed.[1]

In contrast to many reports on the cationic synthesis of star block copolymers, e.g., $(AB)_3$,[2,3] the preparation of hetero arm star polymers has been challenging due to the lack of appropriate linking agents. Recently, we have developed bis(diarylethylene)s, e.g., 2,2-bis[4-(1-phenylethenyl)phenyl]propane, as living coupling agents to prepare A_2B_2 hetero arm star polymers (A = polyisobutylene (PIB), B = poly(methyl vinyl ether) (PMeVE)).[4] The synthesis involved the living coupling reaction of living PIB$^+$ to yield stoichiometric amounts of bis(diarylalkylcarbenium) ions, which efficiently initiated the polymerization of MeVE. Although A_2B_2 hetero arm star polymers have been successfully prepared by this method, it is difficult to obtain linking agents with functionality greater than 2 to obtain A_nB_n hetero arm stars with $n > 2$. In this communication we present a new facile route to prepare A_3B_3 (A = PIB, B = PMeVE) hetero arm star copolymers.

Experimental Section. a. Materials. 1,3,5-Tricumyl chloride (TriCumCl) and 2-PIB-furan (2-PIB-Fu) were synthesized according to the literature.[5,6] The purification of 2,6-di-*tert*-butylpyridine (DTBP), methyl vinyl ether (MeVE), hexanes (Hex), and CH_2Cl_2 have been described.[6] Titanium(IV) chloride ($TiCl_4$, 99.9%, Aldrich) and titanium(IV) isopropoxide ($Ti(OiPr)_4$, 99.999%, Aldrich) were used as received.

b. General Reaction Procedure. All reactions were carried out in large test tubes under a dry ($[H_2O] < 5$ ppm) nitrogen atmosphere in an Mbraun 150-M glovebox (Innovative Technology Inc.). 2-PIB-Fu, DTBP, and TriCumCl were mixed in Hex/CH_2Cl_2 40/60 (v/v) at −80 °C, followed by the addition of $TiCl_4$ to commence the linking reaction. The concentrations were $[\text{TriCumCl}] = 1 \times 10^{-3}$ M, $[\text{2-PIB-Fu}] = 3 \times 10^{-3}$ M, $[TiCl_4] = 4 \times 10^{-2}$ M, and $[\text{DTBP}] = 3 \times 10^{-3}$ M. Upon the completion of the linking reaction (3 h) $Ti(OiPr)_4$ ($[Ti(OiPr)_4] = 2.8 \times 10^{-2}$ M) was added followed by the addition of MeVE ($[\text{MeVE}] = 0.1$ M). The temperature was raised to 0 °C, and after 15 h the polymerization of MeVE was quenched with prechilled methanol. The samples were poured into 10% ammoniacal methanol and dried under a hood. The products were dissolved in CH_2Cl_2, and the solution was filtered through a filter paper to remove inorganic salts. The solvent was evaporated, and the product was dried in a vacuum oven.

c. Chromatography. The crude A_3B_3 product was analyzed by thin-layer chromatography (TLC) using silica gel as a stationary phase. Combinations of Hex and tetrahydrofuran (THF) were used as mobile phases. Two spots were obtained when pure Hex, a good solvent for PIB, was used because only linked triarm star PIB traveled on the TLC film. Four spots were observed in Hex/THF 70/30 (v/v), which indicated that A_3B_3, A_3B_2, A_3B_1, and A_3 could be separated. R_f (retention factor) was increasing in the order $A_3B_3 < A_3B_2 < A_3B_1 < A_3$ (0, 0.44, 0.56, 1).

d. Characterization. Molecular weights were measured at room temperature with a Waters HPLC system equipped with a model 510 HPLC pump, a model 410 differential refractometer, a model 441 UV−vis detector, an on-line multiangle laser light scattering (MALLS) detector (laser wavelength = 690 nm), (MiniDawn, Wyatt Technology Inc.), a model 712 sample processor, and five Ultrastyragel gel permeation chromatography (GPC) columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as a carrier solvent with a flow rate of 1 mL/min. Refractive index increments (d*n*/d*c*) of star copolymers were calculated from the individual d*n*/d*c* of PMeVE (0.063)[7] and PIB (0.109)[8] based on their relative compositions determined by ^{1}H NMR spectroscopy. ^{1}H NMR spectroscopy for structural analysis was carried out on a Bruker 250 MHz spectrometer using $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) as a solvent.

Results and Discussion. We have recently reported the quantitative addition of ω-furan functionalized PIB (2-PIB-Fu), obtained from a simple reaction between living PIB and 2-Bu_3SnFu, to living PIB in Hex/CH_2Cl_2 40/60 (v/v) at −80 °C in conjunction with $TiCl_4$. The resulting living coupled PIB-Fu$^+$-PIB′ was successfully employed for the subsequent polymerization of MeVE to yield poly(IB-*s*-IB′-*s*-MeVE) hetero triarm star copolymer. Conceivably, in place of living PIB a multifunctional cationic initiator could be used to efficiently link *n* arms of 2-PIB-Fu and retain *n* cationic charges at the core. Subsequent addition and efficient initiation of a second monomer are expected to yield A_nB_n hetero arm star copolymer. Since TriCumCl has been employed in numerous efficient syntheses of star homo or block copolymers[2,3,9] in conjunction with $TiCl_4$, we have selected TriCumCl for the linking of 2-PIB-Fu as illustrated in Scheme 1a. Upon addition of $TiCl_4$ to the reactor charged with a stoichiometric amount of 2-PIB-Fu and TriCumCl, a transparent and stable yellow color developed due to the generation of stable carbenium ion on the furanyl ring. To monitor the linking reaction, aliquots of the reaction mixture were withdrawn from the reactor at various times, quenched with prechilled methanol, and analyzed by ^{1}H NMR spectroscopy and GPC. The ^{1}H NMR spectrum in Figure 1 shows that the three resonance signals (6.0, 6.3, and 7.4 ppm) due to the inequivalent protons on the furanyl ring in 2-PIB-Fu completely disappeared, and a single signal appeared at 5.8 ppm attributed to two chemically equivalent protons in the furanyl ring. GPC traces of the original

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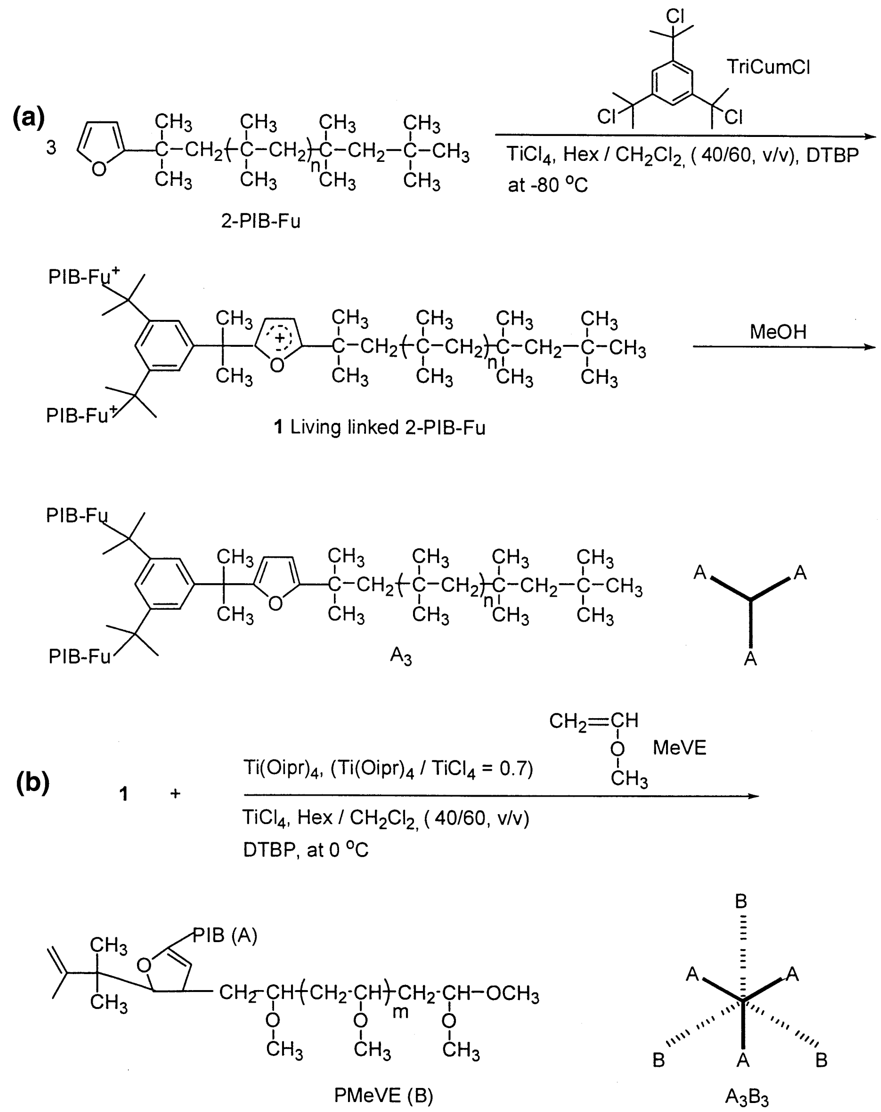
Scheme 1



2-PIB-Fu and triarm star PIB (A_3) are shown in Figure 2. The linked product exhibited approximately tripled molecular weight of the precursor 2-PIB-Fu, and lower polydispersity index (PDI), indicating quantitative linking.

After the successful linking reaction, the polymerization of MeVE was investigated according to Scheme 1b. Linking was followed by the addition of $Ti(OiPr)_4$ to reduce the Lewis acidity using a $[Ti(OiPr)_4]/[TiCl_4] = 0.7$ ratio, which is optimal for the polymerization of MeVE.[6] After tuning the Lewis acidity, MeVE was introduced to the reactor, and the temperature was increased to 0 °C to accelerate the polymerization of MeVE. As the polymerization proceeded, the transparent yellow color of the solution gradually vanished. After 15 h, the polymerization was quenched with prechilled methanol (conversion of MeVE ~90%). The GPC RI trace (Figure 2) of the crude A_3B_3 shows a hump on the lower molecular weight side, which indicates that the crude product contains star polymers with different numbers of arm. The crude product gave four spots with Hex/THF 70/30 (v/v) as eluent on a thin-layer chromatographic (TLC) plate. With pure Hex as eluent, the R_f value of the linked PIB and a mixture of A_3B_3, A_3B_2, A_3B_1 was 1 and 0, respectively. Based on this information, column chromatography of the crude product was carried out on silica gel. First, the linked triarm star PIB (A_3) was eluted with pure Hex. By changing the eluent to a Hex/THF 70/30 (v/v) mixture, A_3B_1 ($R_f = 0.56$) was collected followed by A_3B_2 ($R_f = 0.44$). Finally, the target material $A_3B_3$was recovered using pure THF. The fractions are shown in Table 1.

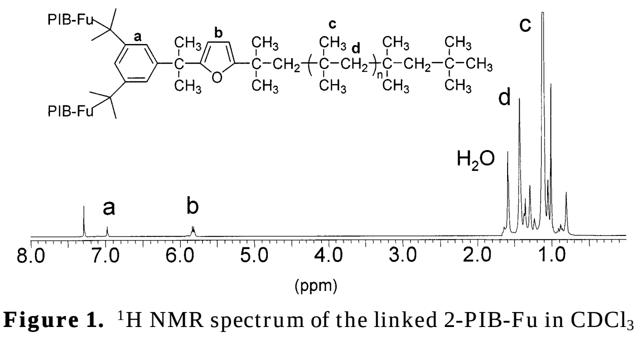


Figure 1. ^1H NMR spectrum of the linked 2-PIB-Fu in $CDCl_3$.

Based on the weights of the fractions, the crossover efficiency was approximately 63%. The architecture of A_3B_3, i.e., that it carries six arms, was confirmed by GPC. Figure 2 shows that the total molecular weight of PMeVE in A_3B_3 is approximately 3 times that of one arm of PMeVE in A_3B_1. The majority of the side product

Table 1. Column Chromatography on Silica Gel of the Crude A_3B_3 Hetero Arm Star Copolymers[a]

no.	eluent	vol (mL)	W_{pi} (g)	ΣW_{pi} (g)	% W_{pi}	ΣW_{pi} (%)	M_n (PDI)
1	Hex	20	0.0007	0.0007	0.21	0.21	
2	Hex	20	0.0349	0.0356	10.45	10.67	2700 (1.1)
3	Hex	20	0	0.0356	0	10.67	
4	Hex/THF[b]	20	0	0.0356	0	10.67	
5	Hex/THF[b]	20	0	0.0356	0	10.67	
6	Hex/THF[b]	20	0.0003[c]	0.0359	0.09	10.75	
7	Hex/THF[b]	20	0.0039[c]	0.0398	1.17	11.92	5100 (1.1)
8	Hex/THF[b]	20	0	0.0398	0	11.92	
9	Hex/THF[b]	20	0.0013[d]	0.0411	0.39	12.31	
10	THF	20	0	0.0411	0	12.31	
11	THF	20	0.089	0.1301	26.65	38.96	11000 (1.2)
12	THF	20	0.1890	0.3191	56.59	95.59	11000 (1.2)
13	THF	20	0.0013	0.3204	0.39	95.94	

[a] Total amount of polymer loaded in the column: 0.334 g. W_{pi}: the weight of the polymer in sample *i* recovered from the column. [b] Hex/THF 70/30 (v/v). [c] These fractions were combined to determine M_n. [d] The composition of no. 9 (A_3B_2) was confirmed by the R_f on TLC because the concentration was below the range of the detection by GPC.

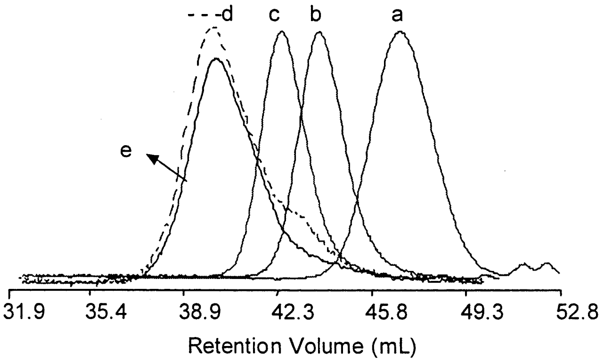


Figure 2. Overlaid GPC RI traces of (a) the precursor 2-PIB-Fu ($M_n = 800$, $M_w/M_n = 1.2$), (b) the linked product ($M_n = 2700$, $M_w/M_n = 1.1$), (c) poly(isobutylene$_3$-*star*-methyl vinyl ether$_1$) ($M_n = 5100$, $M_w/M_n = 1.1$), (d) crude poly(isobutylene$_3$-*star*-methyl vinyl ether$_3$), and (e) purified poly(isobutylene$_3$-*star*-methyl vinyl ether$_3$) ($M_n = 11\,000$, $M_w/M_n = 1.2$). [TriCumCl] $= 1 \times 10^{-3}$ M, [2-PIB-Fu] $= 3 \times 10^{-3}$ M, [$TiCl_4$] $= 4 \times 10^{-2}$ M, [Ti(OiPr)$_4$] $= 2.8 \times 10^{-2}$ M, [DTBP] $= 3 \times 10^{-3}$ M, [MeVE] $=$ 0.1 M, Hex/CH_2Cl_2 40/60 (v/v).

is A_3. The ^{1}H NMR spectrum and GPC trace of the separated A_3 after blocking was identical to that of the product obtained from the linking reaction. To explain why the amount of A_3B_2 and A_3B_1 is negligible although that of A_3 is about 10% of the total weight, we offer the following rationalization. After linking the three cationic sites are buried in the core of A_3. Since MeVE is not a good solvent for PIB, we assume that the local concentration of MeVE at the core is lower than in the bulk. If one site does initiate, however, the polarity of the exterior of the core changes, which may increase the diffusion of MeVE to the core allowing initiation by the second site, which in turn leads to an increased initiation rate by the third site. This cooperative behavior may explain the observed “nothing or everything” phenomenon.

Conclusion. In conclusion, we presented a general and efficient synthesis of triarm star homo PIB (A_3) and A_3B_3 hetero arm star copolymers. To the best of our knowledge, this is the first example of an A_3B_3 hetero arm star copolymer. The method can be extended to A_nB_n with $n > 3$ by employing multifunctional living linking agents. Efficient multifunctional cationic initiators carrying 3,[2] 4,[10] 6,[11] and 8[12] initiating sites, already reported in the literature, are primary candidates as linking agents. The micellar properties of A_3B_3 hetero arm star copolymer in comparison to that of A_2B_2 hetero arm star and AB diblock copolymer in water will be discussed in a forthcoming paper.

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